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Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low Pressure Unimolecular Reaction.

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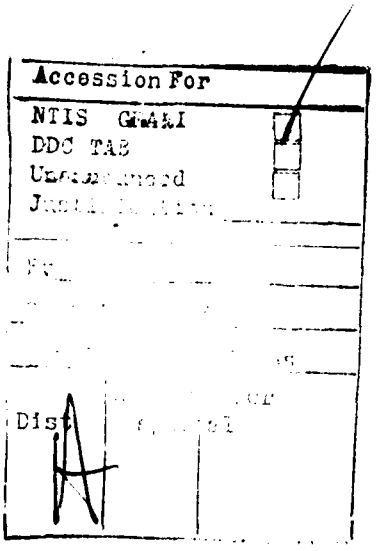

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The Variable Encounter Method was applied to the study of the transient region in vibrational accommodation of reacting cyclopropane at surfaces. Collision efficiency declines with rise of temperature. Surface collisions are more efficient than binary gas phase encounters but $\langle \Delta E \rangle$ declines with rise of temperature. The results agree with an independent earlier study we have made on cyclopropane-d_2.

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Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low Pressure Unimolecular Reaction

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Abstract

A technique has been developed, called the Variable Encounter Method, for the study of gas-wall vibrational energy transfer in the transient region of a unimolecular reaction. The method was applied to the isomerization of cyclopropane to propylene. Molecules at room temperature were introduced into a hot reactor and the accommodation to the final temperature of the reactor was monitored by measurement of the amount of reaction that occurred at various intervals during the energy relaxation process. Specifically, the amount of reaction following some (variable) mean number of collisions, m , between gas and reactor wall was measured. Temperatures in the range 900K-1125K were employed. Reactors having m values of 2.6, 8.5 and 27.2 were used. The average probability of reaction per collision, $\overline{P}_c(m)$, for a given reactor, was deduced from the data and compared with a theoretical stochastic calculation based on both gaussian and exponential models for the energy transfer probabilities. It is found that the efficiency of a seasoned quartz wall is greater than gas-gas collisions of substrate, and that the efficiency declines with increase of temperature. The steady state is closely approached (90%) in a comparatively small number of gas-wall collisions — 10-20, approximately.

Introduction

Lindemann inspired the modern, systematic study of unimolecular reactions.[1] His mechanism proposed that molecules become vibrationally excited by collisions with other molecules, thereby establishing a population of critically energized molecules which may decompose to products if not deactivated by collisions. From this simple mechanism, the study of energy transfer in unimolecular reactions evolved.[2] At sufficiently low pressures, the rate of a thermal unimolecular reaction becomes the rate of critical energization of reactant molecules. The rate of energization depends upon the nature of the collision partners.[3] The study of energy transfer is important both for practical and theoretical reasons. In thermal systems, such study has almost invariably been carried out under steady state conditions.

The present report describes a study of energy transfer in a unimolecular reaction in which molecules experience collisions only with the wall of the reaction vessel. The objective was to study the energization process in the transient region prior to the establishment of a steady-state population of energized molecules. A stochastic treatment has been applied to unimolecular reactions by Shuler and Rubin and by Montroll and Shuler.[4] Treatments of the "mean first passage time" (the average time required for a random walker to reach an absorbing barrier along an energy coordinate) have been developed by Kim[5] and Widom.[6] In principle, if one knows the matrix of transition probabilities among molecular energy levels and the initial population vectors, then one may calculate the mean first passage time and the transient behavior.

There has been very little experimental work done in the transient region. Dove, Nip, and Teitelbaum[7] found an "incubation period," corresponding to ca. 3000 collisions, in the shock-heated N_2O decomposition. In an early VLPP paper, Benson and Spokes[8] claimed that accommodation to an energy of 60 kcal

mole^{-1} occurred in $\sim$ 80 collisions, but the basis of their treatment was inadequate to support their conclusions. In this paper we describe a new method, called the Variable Encounter Method, for the study of the transient region, and its application to cyclopropane isomerization. A preliminary account of the method has been given.[9]

Description of the Method

The Variable Encounter Method (VEM) depends on the random entry of molecules into a hot reactor from a cold reservoir flask, under molecular flow conditions. A molecule leaving the hot zone experiences a large number of collisions with the cold wall of the reservoir before re-entering the reactor. The molecules thus automatically recycle themselves through the reactor. The mean number of hot collisions that a molecule makes per encounter with the hot reactor, m , is a function of the shape of the hot zone. One may easily measure rather small reaction probabilities per encounter by using large experimental times.

Certain design features of the experiment are important. The ratio of cold surface area to hot surface must be sufficiently large to ensure that a molecule is cooled between encounters. The mean free path must be much larger than the reactor dimensions. The pressure must be low enough so that the system is well into the fall-off region (ideally, in the second order region). The mean free flight time between wall collisions in the hot zone should also be as large as possible compared to the mean reaction time of the activated molecules. Of course, the final exit flight involves a longer path length into the cold flask. The total amount of gas and the percent reaction are to be commensurate with the sensitivity of the analysis method.

The relation between amount of reaction and the experimental time is

$$-\ln(R_t/R_o) = k_{obs}t \qquad (1)$$

where R_t is the amount of reactant at time t, and R_o is the initial amount of reactant. The experimental rate constant k_{obs} is related to the average probability of reaction per collision, $\bar{P}_c(m)$, for a given (m) reactor, and to the rate of entry of molecules from the reservoir into the reactor; the latter

involves only simple mechanical and gas kinetic quantities.

The mean number of collisions m, per encounter, was calculated by a Monte Carlo method modeled on that of Davis,[10] and the principle of the calculations is reviewed in ref. 11. The cosine law of reflection was employed and is believed to be the appropriate model under the present condition. The cosine law distribution is characteristic of diffuse as opposed to specular reflections at a surface. The seasoned quartz surface employed is assumed to be microscopically rough. Microscopic roughness, as well as high temperatures, usually lead to diffuse scattering.[12] In any case, since initial entry into the hot reactor does follow a cosine law, even the extreme assumption of specular reflection thereafter, for the reactor shapes described in the Experimental section, does not greatly perturb the calculated values of m (1-2 units in the range m = 10 to 30).

Along with m, the distribution of collisions and mean distance between collisions were also calculated.

Experimental

The apparatus consisted of a 2-liter fused quartz reservoir sphere on to which were blown several cylindrical closed finger reactors of diameter 3.2 cm. The quartz bulb was connected to the system by a ground joint, which permitted each of the reactors to be rotated into position for heating. In order to heat a reactor, it was imbedded in a stainless steel block surrounded by a temperature-controlled furnace. Several thermocouples were cemented to the heated finger so that the temperature along the reactor could be monitored. Temperature fluctuation along the length of the finger amounted to less than 10° over most of the length.

The length of a particular finger determined the mean number and distribution of collisions that a molecule made on entering the reactor. Two types of reactor apertures were used; the first being the unconstricted opening to the reactor, and the second being a blown circular constriction at the entrance to the cylinder. Reactors having m values of 2.6, 8.5 and 27.2 were used. Some data were collected in an m = 107 reactor, but were more fragmentary; they are also believed to be less reliable, because the reactor was apparently not as well seasoned, and are not included here.

The relative sizes of the quartz sphere and the aperture of an attached reactor were such that the internal surface area of the sphere was more than one hundred times the aperture area. Thus, after an encounter, molecules were cooled before re-entering the hot reactor.

The quartz sphere was attached to a glass vacuum system that could be pumped below 10^{-6} torr. Provision existed for gas handling and measurement, sample introduction, and transfer to the analytical system.

Reaction mixtures were analyzed by gas chromatography. A squalane (28% on Chromosorb P) and phenyl isocyanate - Porasil C series column arrangement

was used. In this arrangement, propene was eluted before the parent cyclopropane, with a concomitant advantage in sensitivity.

Cyclopropane (Matheson reagent, 99.0% min.) was used, usually without further treatment for most experiments. Analysis revealed 0.3% propene as an impurity. For some experiments involving low percent reaction, the propene was reduced below 0.05% by passage through a $HgSO_4$-H_2SO_4 column (1 cc of a 20% $HgSO_4$-20% H_2SO_4 aqueous solution per gram of Chromsorb W).

To perform a run, a measured aliquot of cyclopropane was admitted into the 2-liter quartz bulb for a given time, after which the reaction mixture was pumped out through a liquid nitrogen-cooled trap. The time required to pump out the vessel to 1/e of the initial pressure (~ 10 sec) was entered into the run time with suitable weighting. Run pressures in the bulb ranged from 10^{-4} to 10^{-3} torr Hg. Run temperatures ranged from 900 K to 1126 K, and reaction times from 25 seconds to 4 hours.

Results and Discussion

Experimental data were obtained by measuring the percent isomerization as a function of time, for each reactor at each temperature. In most cases, three separate runs were made at a given run time, and three or four run times were used so that the determination of the experimental rate constant, and of the value of $\bar{P}_c(m)$, at a given temperature in a given reactor was the result of 9 to 12 runs. Plots of the log of the fraction of reactant remaining vs run time gave straight lines. An illustrative plot is shown in Fig 1 for the reactor m = 8.5, T = 1012 K. The plots were found to be straight lines, as given by eq. (1).

The primary quantity of interest in the present study is the mean probability of reaction per collision in a given reactor, $\bar{P}_c(m)$ (Table I). It is a quantity that is closely related conceptually to stochastic theories of chemical kinetics. Plots of $\bar{P}_c(m)$ vs temperature are shown in Fig 2, for mean collision numbers m of 2.6, 8.5 and 27.2. It is noted that the values of $\bar{P}_c(m)$ tend to converge at lower temperatures, i.e., the wall becomes a stronger collider at lower temperatures.

The corresponding Arrhenius plots give slightly curved lines; there is no a priori reason why the plots should be straight lines in a non-equilibrium system. Average Arrhenius values are given in Table II.

The gas-wall energy transfer process may be described in terms of a probability matrix, where p_{ij} is the element for a molecule going from the j^{th} to i^{th} energy level upon collision. Once the functional form (model) of the downsteps of this matrix is specified, the corresponding upsteps may be calculated by detailed balance. The details of the construction of these matrices are given in ref. 13. Two different models for the probability of a downstep of size ΔE were used.

$$\underline{\text{exponential}}: \quad P_{\Delta E} = A \exp(-\Delta E/\langle\Delta E\rangle); \quad 0 \leq \Delta E \leq 9000 \text{ cm}^{-1}$$

$$= 0 \quad ; \quad \Delta E > 9000 \text{ cm}^{-1}$$

$$\underline{\text{gaussian}}: \quad P_{\Delta E} = A' \exp[-(\Delta E - \Delta E_{mp})^2/2\sigma^2]; \quad 0 \leq \Delta E \leq 9000 \text{ cm}^{-1}$$

$$= 0 \quad ; \quad \Delta E > 9000 \text{ cm}^{-1}$$

where A and A' are normalization constants which also include the upstep probabilities; $\langle\Delta E\rangle$, ΔE_{mp} (mp signifies most probable), and σ are parameters of the model. The limitation of 9000 cm^{-1} is a practical computational feature invoked to make the matrix of more tractable dimensions. The details of how calculated $\overline{P}_c(m)$ curves are obtained from these models of energy transfer are given in ref. 14. Because of the truncation feature, we also define an effective value of the average energy downstep, called $\langle\Delta E'\rangle$.

In all cases, the values of $\langle\Delta E\rangle$ or ΔE_{mp} were selected to fit the m = 2.6 reactor data, and $\overline{P}_c(m)$ values were then calculated for the other, larger, m reactors. The reason for this procedure is that the calculated value of $\overline{P}_c(m)$ is somewhat more sensitive to the value of $\langle\Delta E\rangle$, or ΔE_{mp}, for smaller m values. The values of $\langle\Delta E'\rangle$ and ΔE_{mp} used at various temperatures are given in Table III. It is seen that the amount of energy transferred upon collision is quite large (approaching strong collider) at lower temperature and decreases at higher temperatures (Table III). A decrease in efficiency with temperature has previously been observed in neat gas experiments[15] where the ΔE values are significantly smaller. This same decrease has been observed in other VEM work[9,14] and in some low pressure pyrolysis studies.[16] The ΔE values reported here are somewhat higher than those found for cyclopropane-d_2[14] (Table III). The difference is systematic, but within experimental error at the higher temperatures. The experimental procedures used here in early work, particularly seasoning, may have been somewhat less reliable than in the other studies. The present value is noticeably higher at 900K although still qualitatively and semi-

quantitatively consistent. It is seen from the lack of fit at 900K that an exponential model is not as appropriate as a gaussian model for very strong collisions. This is a well-founded conclusion.[13]

Conclusions

The results of the VEM experiments for cyclopropane indicate: a) below 900 K, vibrational energy accommodation is substantially complete in $\sim$ 10 collisions; at higher temperatures, larger collision numbers are necessary for complete accommodation; b) wall collisions are more efficient than gas phase[15] collisions, with wall collisions approaching strong collider behavior at lower temperatures; c) collisional efficiency and $\langle\Delta E\rangle$ decline with increasing temperature, supporting similar findings from the homogeneous cyclopropane-d_2 system.[15]

Acknowledgements

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Table I. Average Probabilities of Reaction per Collision, $\bar{P}_c(m)$

m	T(K)	$\bar{P}_c(m)(x10^8)$
2.6	907	2.71
	993	9.40
	1081	40.4
8.5	891	7.1
	895	6.6
	931	15.8
	1012	65
	1117	512
27.2	906	11.0
	989	86
	1126	1650

Table II. Observed Activation Energies

m	E_a(kcal mole^{-1})
2.6	30
8.5	39
27.2	47

Table III. Average Values of $\langle \Delta E' \rangle$ (cm^{-1}) for Cyclopropane-Wall Collisions

T(K)	900	1000	1075
Gaussian (σ=0.35 ΔE_{mp}[a])	4900 3200[14]	3275 3000[14]	3000 2775[14]
Exponential	b 3035[14]	3100 2775[14]	2850 2425[14]

a) ΔE_{mp} is same as $\langle \Delta E' \rangle$ within a few cm^{-1}.

b) Exponential model too inefficient; cannot give fit.

References

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1. F. A. Lindemann, Trans. Faraday Soc., 17, 598 (1921).
2. D. C. Tardy and B. S. Rabinovitch, Chem. Rev., 77, 369 (1977).
3. D. J. Wilson and H. S. Johnston, J. Am. Chem. Soc., 75, 5763 (1953).
4. E. W. Montroll and K. E. Shuler, Adv. Chem. Phys., 1, 361 (1958).
5. S. K. Kim, J. Chem. Phys., 28, 1057 (1958).
6. B. Widom, J. Chem. Phys., 31, 1387 (1959); 34, 2050 (1961).
7. The recent work of J. E. Dove, W. Nip, and H. Teitelbaum, XVth Int. Symp. Combust., The Combustion Institute, 1975, p. 903-16, is an exception.
8. S. W. Benson and G. N. Spokes, J. Am. Chem. Soc., 89, 2525 (1967).
9. D. F. Kelley, B. D. Barton, L. Zalotai and B. S. Rabinovitch, J. Chem. Phys., 71, 538 (1979).
10. D. H. Davis, J. Appl. Phys., 31, 1169 (1960).
11. B. D. Barton, Ph.D. Thesis, University of Washington, Seattle, 1979.
12. S. T. Ceyer and G. A. Somorjai, Ann. Rev. Phys. Chem., 28, 477 (1977).
13. D. C. Tardy and B. S. Rabinovitch, J. Chem. Phys., 45, 3720 (1966).
14. D. F. Kelley, L. Zalotai and B. S. Rabinovitch, Chem. Phys. in press.
15. I. E. Klein and B. S. Rabinovitch, Chem. Phys., 35, 439 (1978).
16. R. Gilbert and K. D. King, private communication.

Figure Captions

Figure 1 Experimental decay curve at m = 8.5, T = 1012 K

Figure 2 Dependence of $\overline{P}_c(m)$ on T, for reactors of varying m; dotted curves are simple exponential, and dashed curves are simple gaussian calculated curves for values of $\langle \Delta E \rangle$ and ΔE_{mp}, as in Table III, fitted to the m = 2.6 curve.

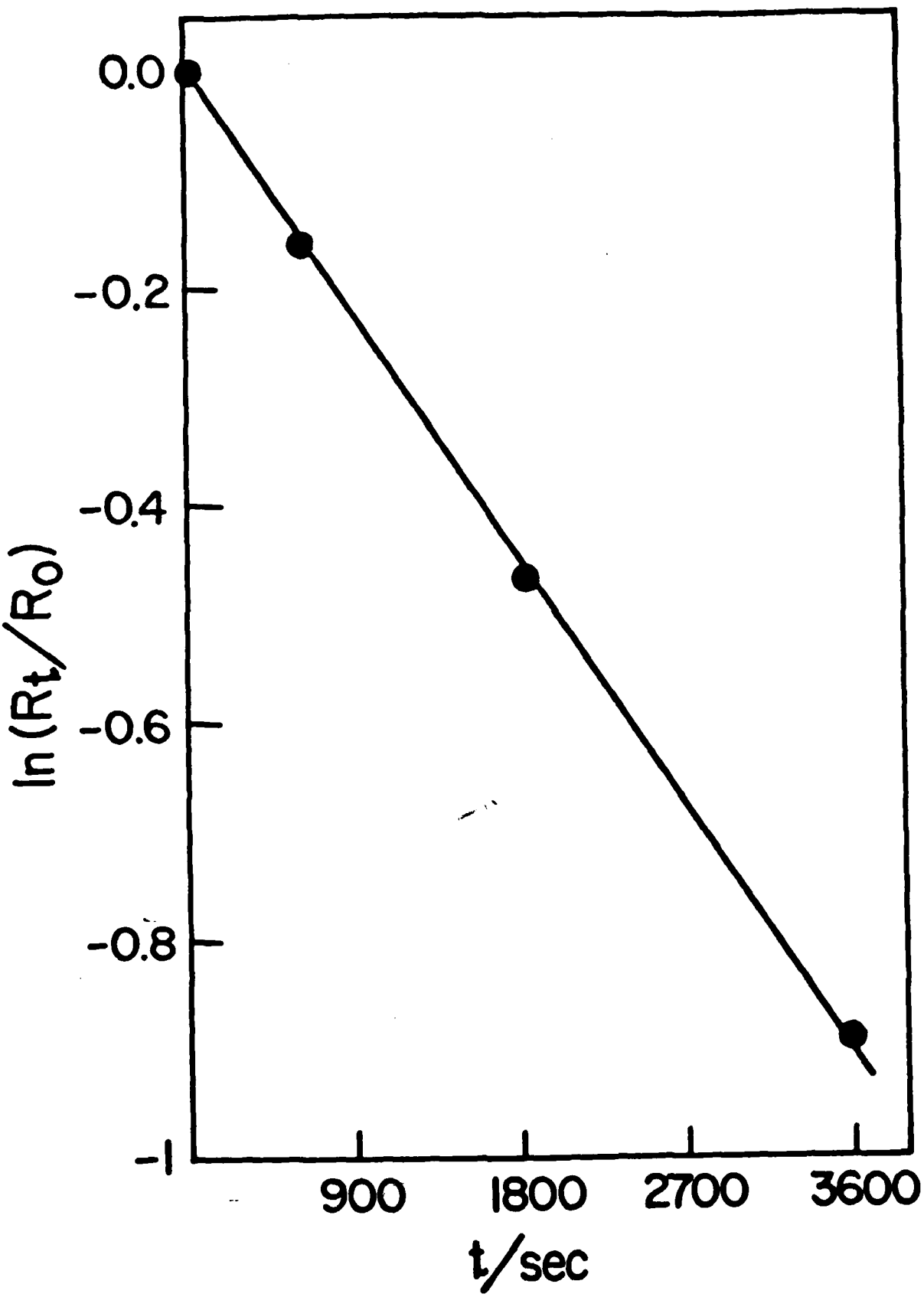

Fig. 1

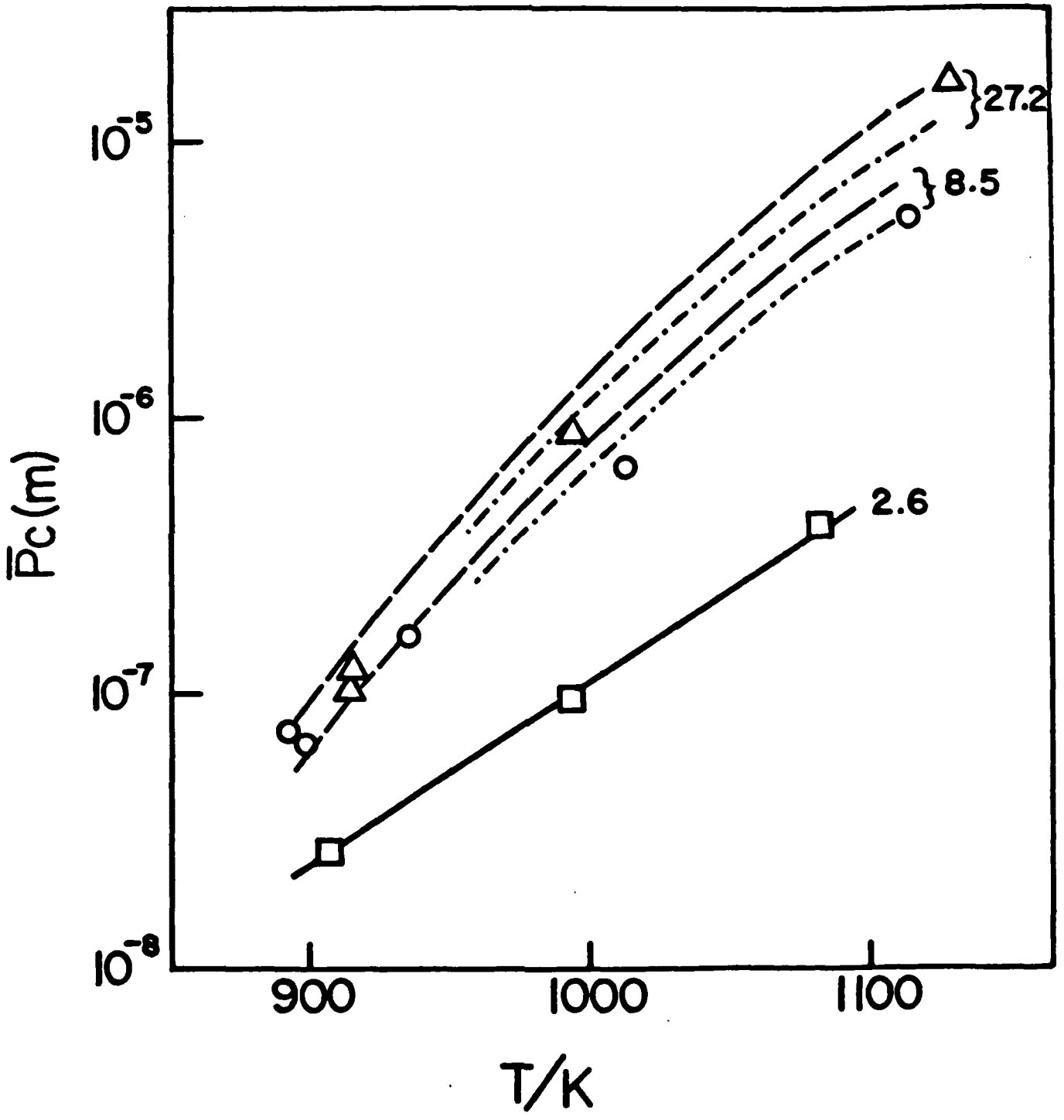

fig 2 Barton et al